



135956

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL RESEARCH LABORATORY
ATHENS, GEORGIA 30613

August 31, 1988

Ms. Ruth Rzepski
Enforcement Project Manager
U.S. EPA, Region III
841 Chestnut Street
Philadelphia, PA 19107

Dear Ms. Rzepski:

The purpose of this letter is to respond to your request for technical assistance and expert opinions as to possible degradation processes which can occur at the AVTEX Fibers site. Drs. Jackson Ellington and James Martin reviewed the Remedial Investigation Report as well as the July 28, 1988 Memorandum from M.C. Ruth, Geraghty and Miller, Inc., to Avtex Fibers regarding clean-up criteria. In addition, they attended, at your request in a letter dated August 18, the August 19 meeting at your office with the Responsible Parties. Their suggestions and/or concerns are provided in the attached document.

I hope that you find the information useful. If there is any other assistance that the Center can provide, please contact us.

Sincerely yours,

Robert B. Ambrose, Jr.

Robert B. Ambrose, Jr., P.E.
Manager, Center for Exposure Assessment
Modeling

Enclosure

cc: J. Ellington
J. Martin

AR304171

Preliminary Evaluation of Degradation
Pathways at the Avtex Fibers, Front Royal Site

Drs. Jackson Ellington and James Martin, P.E.
USEPA Center for Exposure Assessment Modeling
Athens, GA

Based on the preliminary evaluation of: the available sections of the Remedial Investigation Report (Sections 3.0-6.0); the two July 28, 1988 Memorandums from M.C. Ruth, Geraghty and Miller, Inc., to Avtex Fibers regarding clean-up criteria and hydrolysis reactions; and, the August 19 meeting at your office with the Responsible Parties, we offer the following concerns and/or suggestions:

I. Degradation:

1.0. Kinetic Analysis.

1.1 The Remedial Investigation Report (RI), Section 5.0, contained a kinetic analysis based upon measured concentrations of CS₂ in viscose basins 1,2,7,9, 10 and 11 and their known periods of disposal (Table 5.1). These data were used to estimate a degradation rate of 0.33 year⁻¹, indicating that the CS₂ in the basins would degrade with a half-life of approximately 2.1 years. The rates were then used to estimate maximum CS₂ concentrations in each of the basins following a period of 5 and 10 years, as described in the RI and the July 28, 1988 Memorandum from M.C. Ruth, Geraghty and Miller, Inc., to Avtex Fibers regarding clean-up criteria.

1.2. The approach described would seem reasonable in that it would provide an indication of the rate of degradation, irrespective of the degradation processes. However, the data used in the study are not considered to be sufficient to support such a calculation for the following reasons:

a. The method should be applied to the degradation of the total mass of materials in the basins rather than concentrations. The limited data available suggests strong vertical gradients in CS₂ concentrations in each of the basins. If these gradients were well characterized, the total mass of material in the basins could be calculated by integrating the spatially varying concentrations over depth. However, the limited number of samples are insufficient to characterize these gradients or allow this calculation. Therefore, the mass of CS₂ and other materials present in the basins remain unknown.

b. Data from section 3.0 of the RI suggests that horizontal gradients may also be expected. The covered basins are deepest and most highly saturated near their center. The RI suggests that the extent of the basins in the horizontal may be larger than indicated in plant diagrams and that some material may have moved to shallow deposits outside of the basin boundaries. No information is available to estimate the near surface horizontal variability of CS₂ and other contaminants.

c. The concentrations of CS₂ on which the calculations were based were taken at differing depths in the basins with respect to the viscose materials. Samples were compared which were within the viscose materials, or in areas of transition between the viscose materials and the underlying substrate or the

AR304 172

overlying cap for the covered basins. Therefore, the observed concentrations may be required in order to quantitate the contaminant mass.

1.3. It would be suggested that further clarification be obtained as to the rationale for selecting the sampling locations and why more extensive sampling of the cores was not conducted to quantitate vertical profiles. Perhaps if the cores are preserved additional quantitation may still be possible for some materials. Where this is not possible, it is suggested that further sampling may be required in order to quantitate the contaminant mass.

1.4. The apparent profiles suggest that considerable spatial variation may be expected in the degradation rates. For example, variations in pH and temperature with depth would impact hydrolysis rates, while near surface transport will affect volatilization rates.

1.5. The CS_2 mass, if accurately determined, may serve only as an indication of the extent of degradation. The CS_2 probably does not represent a distinct mass placed in the basin which degrades over time, but a reaction product. The primary source of CS_2 in the basins is believed to be the decomposition of cellulose xanthates. Conversely cellulose xanthate is regenerated by the presence of CS_2 in the viscose.

1.5.1. The mass of CS_2 present may only represent a fraction of the total mass that may be produced during the decomposition of the xanthates.

1.5.2. If other processes, such as hydrolysis, are as fast as the current literature seems to indicate, it may be possible that the CS_2 measured analytically may have been that produced by xanthate decomposition during the purge and trap analysis of the samples rather than the amount actually present in situ.

1.6. Not only the rate of removal but the removal processes themselves should probably receive attention. For example, if hydrolysis controls, sulfides may be produced which may affect metals mobility. If volatilization is a major removal processes, then atmospheric loading may be of concern. Some possible pathways are discussed in the following sections.

2.0. Flushing.

2.1. In their July, 1988 Memorandum, it was suggested that the near surface removal of CS_2 from basin 10 following dewatering was possibly due to flushing action by rainwater.

2.2. The flushing of CS_2 from the near surface layer is a possible mechanism of removal. However, other processes, such as volatilization, may be occurring. The identification of the dominant loss mechanism may be of importance in evaluating exposure pathways.

2.3. Some flushing is also expected to occur through the basins and into the groundwater. For the closed basins the RI (section 3.0) indicated that the permeability of the cap is greater than of materials adjacent to the basins and that the caps slope towards their centers and capture rainfall. Further, the viscose has a permeability which increases fluid accumulation during periods of rainfall. Similarly, for the uncovered basins, the large void spaces which were

characterized for the viscose solids should allow leaching of materials to the aquifer. The extent of the contamination in the water table appears to be well characterized in the RI.

3.0 Volatilization.

3.1. Volatilization may be a major pathway for contaminant removal, both from the basins and during the dewatering process. Volatilization will act both as a source of removal of CS_2 from the basins and a source of contamination to the atmosphere. Atmospheric loading is expected to occur during the dewatering process as well as from the undisturbed basins.

3.2. Volatilization from the material removed during dewatering would be expected to be rapid. For atmospheric loading, a conservative estimate of the releases to the atmosphere may be obtained by assuming that the water removed is saturated with CS_2 and that it is immediately volatilized. At a pumping rate of 50 gpm, this would result in a flux to the atmosphere of approximately 73 lb/hr. If actual dissolved concentrations are less than the loading would be proportionately reduced.

3.2.1. The 73 lb/hr is considerably less than that stated to be normally released from the manufacturing process (5000 lb/hr), and from that perspective may be considered a minor source. However, it is not shown that the 5000 lb/hr is inconsequential. Additionally, the dewatering is expected to result in a source at ground level, while the releases from the plant may occur from a stack located some distance from ground level. Therefore, it may be appropriate to consider the source of dewatering and its consequences independent of other sources.

3.2.2. The argument that only company employees and their contractors will be exposed to the contamination should be considered in the context of EPA regulations.

3.2.3. In addition, the spatial extent of the atmospheric effects are not known. Some estimates of the extent of atmospheric effects could probably be made using available modeling techniques. In order to determine the appropriate techniques it must first be decided if long or short term effects are critical. For example, atmospheric instabilities may be more of an issue if the short term effects of exposures are considered.

3.2.4. It should be encouraged atmospheric concentrations of contaminants be monitored during the dewatering process, as well as concentrations in the removed water at several steps within its treatment process. Plans should also be made to determine concentrations in the basins before and following dewatering, if possible, in order to estimate its effects.

3.2.5. Releases of other materials may be expected during dewatering. For example, metals in the viscose materials are possibly bound as insoluble sulfides. However, when the anaerobic conditions and pH is changed, such as during dewatering or groundwater leaching, the metals may be released.

3.3. Volatilization from the basins is also expected to be a loss mechanism. However, the loss rate is expected to be limited by transport in the liquid rather than by the gas layers.

AR304174

3.3.1. For example, for the liquid layer the volatilization rate may be on the order of 0.1 m/day, which for a 10 ft (3.05 m) deep water layer would result in a degradation with a half-life on the order of 21 days. The rate for lower layers would be expected to be less due to the decreased transport rates. However, for the near surface after compaction, volatilization may be rapid.

3.3.2. Volatilization could contribute to the apparent vertical gradations in concentrations, if these concentrations are considered realistic. The RI report indicates that the cover material is more porous than the surrounding solids and that the waste viscose solids is characterized by a solid matrix with large void spaces capable of holding large volumes. This would not preclude volatilization from being a major loss mechanism.

4.0. Biodegradation.

4.1. The material in the basin may degrade because of biological activity. However, the extremes of pH would indicate that biological activity would be localized with the greatest activity occurring as the pH approaches 7. The least activity would be expected near the bottom of the pits where the pH approaches 11.

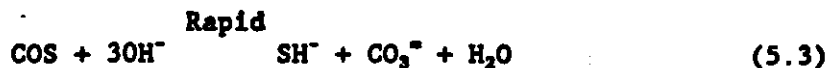
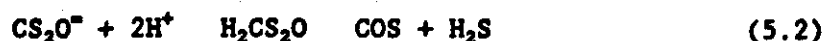
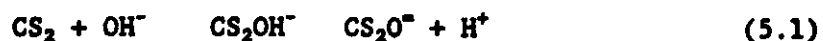
4.2. Biological activity may be indicated by a reduction in the lengths of polymer chains over time. Biological activity can also be verified by simply examining the wastes for the presence of bacteria and then determining if those bacteria are able to degrade the major waste components and determine the rates of degradation. This analysis should be done with samples at varying depths of the basins. If organisms are found, it would be reasonable to assume that the activities could be enhanced to degrade the waste, possibly to biomass plus CO₂. The older ponds would be expected to have the greatest microbial activity. Organisms from the older ponds could be used to inoculate the more recent ponds. The ERL-Athens has an on-going bioremediation research effort which could be utilized to assess a potential biotreatment strategy. The ERL-Athens also has a microbiological fate program which can be accessed to determine the natural degradation rates within the ponds. These programs could be accessed in order to complete the work, or to assist in the design and review of such studies.

5.0 Hydrolysis.

5.1. Under hydrolysis, two separate reactions are important: (1) pH independent decomposition of cellulose xanthate and (2) reaction of carbon disulfide with hydroxide ion.

- a. In viscose, carbon disulfide will be formed by the pH independent decomposition of the cellulose xanthate. Part of the carbon disulfide will react with the cellulosic material to reform cellulose xanthate with the balance consumed by reaction with hydroxide ion. The decomposition rate of cellulose xanthate would be dependent on temperature.
- b. The reaction of carbon disulfide with hydroxide ion is described by the following equations:

AR304175



Equation 5.1 (formation of dithiocarbonate) is assumed to be rate-determining. Half-lives for carbon disulfide of 0.96, 0.48 and 0.22 hours at pHs 9, 10 and 11 respectively were calculated from the report of Gbadebo and Carmichael (Environ. Sci. Technol. 1987, 21, 170-177) on hydroxide ion mediated hydrolysis at 20°C in aqueous buffer.

5.2. Considering only a and b above for carbon disulfide to build up to measureable quantities, the decomposition velocity of cellulose xanthate would exceed the reaction rate of carbon disulfide with hydroxide ion. This would yield an even shorter half-life for cellulose xanthate than carbon disulfide.

Several explanations for the persistence of carbon disulfide in the viscose basins include:

- a. Something in the viscose basin retards the reaction of carbon disulfide with hydroxide ion.
- b. The carbon disulfide measured analytically was produced by xanthate decomposition during the purge and trap analysis of the samples.

II. Recommendations

It is our opinion that the dewatering processes could proceed if monitoring is conducted as recommended above. The additional concerns expressed can be addressed during and following dewatering. However, it is recommended that additional monitoring, laboratory, and perhaps modeling work be done in order to further characterize the materials, their degradation processes and rates, exposure pathways and their associated environmental risk.

The RI and this summary concentrated primarily on CS₂. The concentrations, removal pathways, and effects of other materials require additional investigation. The materials include metals, phenols, and possibly some materials such as sodium which in some places constituted nearly 10 percent of the waste mass.

AR304176